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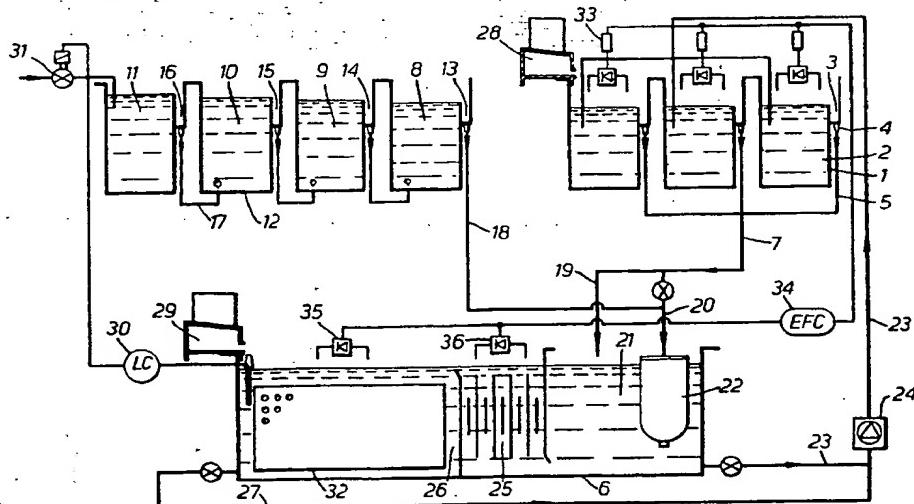
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(54) Process and apparatus for the electrodeposition of nickel

(57) In the electrodeposition of nickel onto articles, a proportion of the nickel electrolyte is continuously removed via conduits 5, 7 from the electrodeposition bath 1, a part of the removed electrolyte is combined with used liquid from the rinsing apparatus 12 (via conduit 18) and passed via conduit 20 through a filter 22 (especially active carbon) for organic decomposition products, and the filtrate is combined in collecting chamber 21 with the remainder of the removed electrolyte via conduit 19. A major proportion of the resulting mixture is returned directly via conduit 23 to the electrodeposition bath. A minor proportion of the mixture is treated in cleaning system 25 to remove metal impurities and then in electrolytic cell 26 to recover excess nickel dissolved in the electrodeposition bath, and is then also returned to the bath via conduit 27. No waste liquid is produced, and evap-

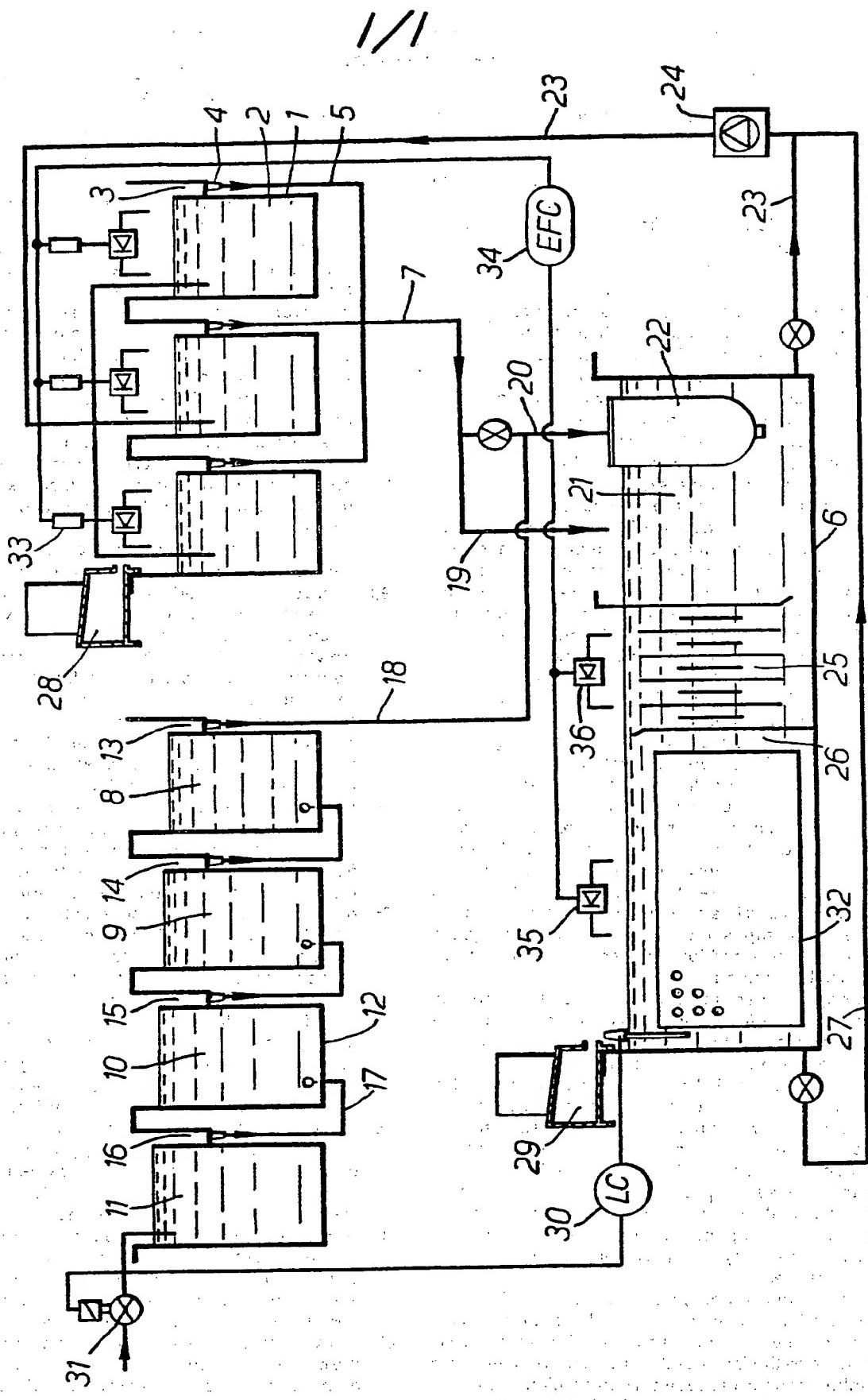
oration losses are counterbalanced by appropriate control of the introduction of fresh rinsing liquid.

Fig. 1



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SPECIFICATION

Process and apparatus for the electrodeposition of nickel

- 5 This invention relates to a process and apparatus for the electrodeposition of nickel, and is concerned with purification of the nickel electrolyte in the electrodeposition bath.
- 10 Electrolytic nickel baths have a wide range of application in industry. Such baths are used predominantly for the electrodeposition of mirror-bright nickel layers on substrates which are then usually provided with a further layer, for example of
- 15 chromium, principally for decorative effect. The nickel layer serves, *inter alia*, to provide a brilliant surface and to smooth out irregularities, such as, for example, abrasion marks. For this purpose organic brighteners are added to the nickel bath. During
- 20 operation, the brighteners give rise to decomposition products which, as their concentration increases, have an adverse effect on the properties of the nickel layer that has been deposited. It is therefore necessary to remove the decomposition products from the bath, or at least reduce their concentration. In the past, that cleaning process was carried out in the majority of cases by stirring active carbon into the bath solution, allowing it to settle, and then pumping out the bath through a filter into a clean
- 25 container. Such a process is labour-intensive and time-consuming. For this reason a process has already been proposed in which the cleaning process using active carbon is effected continuously. In that process, the circulating material is additionally
- 30 passed either completely or partially via active carbon through a filter which serves to remove solid particles of dirt. However, this process has disadvantages. It has been shown that the active carbon, normally present in relatively small quantity, quickly
- 35 agglutinates and it is difficult to control the quantity of the undecomposed brighteners (that is to say, the brighteners required for the operation of the bath), that is to be retained.
- 40 During the operation of the nickel bath not only are the brighteners increasingly associated with decomposition products, but their contamination with foreign metals also constantly increases. This occurs especially in the nickel-plating of hollow bodies, the hollow cavities of which cannot be coated every-
- 45 where with a layer of nickel. Further constituents which militate against complete deposition of nickel are then dissolved out of the base metal. It is possible to remove such impurity constituents with the assistance of the so-called selective cleaning process
- 50 in which the foreign metals are preferentially deposited in an electrolytic cell in a defined current density range.
- 55 Another undesirable phenomenon occurring during operation of an electrolytic nickel bath is the constant increase in the nickel content. That increase is attributed to the fact that the anode current efficiency is higher than the cathode current efficiency, that is to say, somewhat more metal is dissolved at the anode by the electroplating current than is deposited
- 60 at the cathode (the substrate being treated).

The above-mentioned changes in the nickel bath during its operation have, admittedly, little effect in practice, and under some conditions of operation have no effect at all. This results from the fact that

65 every time the treated goods are lifted out of the bath, a certain amount of bath solution, and thus proportionately the troublesome constituents, are removed with them. Before the goods being treated are immersed in the nickel bath, a rinsing process is carried out. The water adhering to the goods and thereby introduced into the nickel bath normally, however, only supplements the evaporation losses arising from operation of the bath at a raised temperature. The quantity of nickel bath solution removed

75 with the goods therefore has to be supplemented by fresh solution. This results in constant renewal of the bath, and its operation is simplified to that extent. The process, however, involves considerable costs: on the one hand, the nickel bath is lost and, on the other hand, the rinsing water which takes up the removed bath solution has to be decontaminated again.

- The present invention provides a process for the electrodeposition of nickel onto articles which are subsequently rinsed, in which a proportion of the nickel electrolyte is continuously removed from the electrodeposition bath, a part of the removed electrolyte is combined with used liquid from the rinsing apparatus and passed through filtration means for reducing the concentration of organic decomposition products, the filtrate is combined with the remainder of the removed nickel electrolyte, a major proportion of the resulting mixture is recirculated directly to the electrodeposition bath, a minor proportion of the said resulting mixture is passed through purification means comprising, in sequence, means for selectively removing impurity metals from solution and thereafter electrolytic means for recovering nickel, the purified solution so obtained is recirculated to the electrodeposition bath, and the introduction of fresh rinsing liquid into the rinsing station is controlled so as to counterbalance evaporation losses in the electrodeposition bath and in the filtration and purification means.
- 100 Preferably, the filtration means for organic decomposition products comprises an activated carbon filter, and such a filter is advantageously so constructed that the solution to be filtered flows therethrough as a result of a geodesic difference in levels.
- 105 In general, the means for selectively removing impurity metals will operate by preferential electrodeposition of the metal(s) concerned.
- 110 Advantageously, the rinsing is effected in a multiple cascade rinsing apparatus, the number of rinsing compartments being sufficient to provide an adequate rinsing action with the amount of rinsing liquid to be used. The rinsing liquid will in general be aqueous, and will normally be de-mineralised water.
- 115 Preferably, the current to the electrolytic nickel-recovery means is so controlled in accordance with the current consumption in the electrodeposition bath that only the excess nickel dissolved in the bath is removed in the nickel-recovery means.
- 120 Advantageously, the cathode elements in the nickel-recovery means are so designed that the
- 125
- 130

- deposited nickel accumulates in the form of discrete pieces, which can readily be re-used in anode baskets in the electrodeposition bath.
- The invention also provides apparatus for the electrodeposition of nickel, which comprises an electrodeposition bath, means for rinsing articles after electrodeposition, means for continuously removing a proportion of the electrolyte in the electrodeposition bath, means for combining a part of the removed electrolyte with used liquid from the rinsing means, filtration means for reducing the concentration of organic decomposition products in the resulting mixture, means for combining the filtrate with the remainder of the removed electrolyte,
- 10 removed electrolyte with used liquid from the rinsing means, filtration means for reducing the concentration of organic decomposition products in the resulting mixture, means for combining the filtrate with the remainder of the removed electrolyte,
- 15 means for recirculating a major proportion of the resulting mixture directly to the electrodeposition bath, purification means for treating a minor proportion of the said resulting mixture firstly to remove impurity metals from the solution and thereafter to
- 20 recover a proportion of nickel electrolytically, means for recirculating the resulting purified solution to the electrodeposition bath, and means for introducing fresh rinsing liquid into the rinsing apparatus so as to counterbalance evaporation losses in the electrodeposition bath and in the filtration and purification means.

The invention enables substantial cost savings to be made in the electrodeposition of nickel.

- Moreover, no waste water or other rinsing liquid
- 30 accumulates from the rinsing process, so that the additional cost of providing a purification plant to decontaminate waste liquid is avoided.

- In addition to enabling liquid removed from the nickel bath to be recirculated, the process of the invention offers the advantage that nickel metal yielded in the electrolytic recovery means can be re-used directly as source metal at the anode. As a result of the preliminary filtration of organic decomposition products and as a result of the selective removal of impurity metals, the nickel metal recovered has at least the same quality as the nickel deposited on the goods being treated.

- The reduction in the concentration of organic decomposition products also increases the efficiency
- 45 of the selective removal of metal impurities.

- One form of process according to the invention, and an apparatus for carrying out the process, will now be described, by way of example, with reference to the accompanying drawing, which is a flow
- 50 sheet, partly in diagrammatic form.

- Referring to the accompanying drawing, a container (1) for the nickel bath is divided into three compartments (2). Each compartment is provided with an overflow channel (3) which permits the level
- 55 of the bath to be held constant. Conduits (5), which merge to form a conduit (7) leading to a purification plant (6), lead from drainage nozzles (4) of the overflow channels (3).

- A multiple rinsing station (12) comprises a series
- 60 of four compartments (8, 9, 10, 11) each having an overflow channel (13, 14, 15, 16, respectively). Rinsing water draining from the overflow channel of the rinsing compartment (11), that is to say, the last compartment in the sequence of operation, flows via
- 65 the duct (17) to the preceding rinsing compartment

(10). Similarly, overflowing rinsing water is conveyed from compartments (10) to compartment (9), and from there into compartment (8).

- The water draining out of the overflow channel
- 70 (13) of the first rinsing compartment (8) is passed via a conduit (18) to the purification plant (6).
- The conduit (7) coming from the nickel bath compartments (2) branches just before the purification plant to form two separate conduits (19) and (20).
- 75 Conduit (19) conveys a relatively large proportion of the nickel bath flowing out of the overflow channels (3) directly to a collecting chamber (21) of the purification plant (6). The conduit (18) coming from the first rinsing compartment (8) communicates with the
- 80 conduit (20) so that the rinsing water draining into the conduit (18) is combined with the relatively small proportion of the nickel bath outflow that passes along the conduit (20), and the resulting mixture is introduced into an active carbon cleaning stage (22)
- 85 in the purification plant (6). The outflow from the cleaning stage (22) is combined in the collecting chamber (21) with the relatively large proportion of the nickel bath outflow that enters from the conduit (19).

- 90 A major proportion of the mixture of nickel bath outflow and rinsing water in the collecting chamber (21) is recycled to the nickel bath compartments (2) via a conduit (23) and a filter (24), which serves to remove solid pollutants. A relatively small proportion, for example, approximately $4 \text{ m}^3/\text{h}$ from a total of approximately $20 \text{ m}^3/\text{h}$, flows out of the collecting chamber (21) into a selective cleaning system (25). In the system (25), foreign metal impurities are preferentially removed by selective electrodeposition. The
- 95 selective cleaning system is followed by an electrolytic cell (26) in which, to offset the increase in nickel content occurring in the electrolytic nickel bath (1), the metal is precipitated from the solution. The cathode blanks (32) of the cell (26) are preferably so
- 100 designed that the metal accumulates in separate small pieces, which permit simple re-use in the anode baskets of the nickel compartments (2). The purified mixture of nickel bath outflow and rinsing water is recirculated to the nickel bath (2) from the
- 105 electrolytic cell via a conduit (27), which joins the conduit (23) before the filter (24). The nickel bath forms the major portion of the mixture since, in the process illustration, only about 60 litres per hour of rinsing water is fed into the last compartment (11) of
- 110 the multiple rinsing station (12). For this purpose, completely demineralised water is preferably used, so that the introduction of impurities is avoided.

- Since the nickel bath solution, both in the working vessel (1) and in the purification plant (6), is normally
- 115 maintained at a temperature of approximately 55°C , the entire amount of rinsing water supplied evaporates. The evaporation effect is reinforced by suction devices (28, 29) which are arranged above the surfaces of the liquids and through which the vaporised water is drawn off. The evaporation losses are automatically counterbalanced by a device (30) which controls a magnetic valve (31) on the rinsing water supply in response to reductions in the liquid level in the plant (6).
- 120 The total amount of electric current consumed in

the electrodeposition compartments of the nickel bath (1) is recorded by ampere-hour counters (33). With this value as the reference variable, the amount of current to be delivered by power supply units (35, 5 36) to the selective cleaning stage (25) and the electrolytic cell (26) can be controlled by means of the device (34). That amount of electric current is advantageously so determined that only the excess nickel is deposited in the electrolytic cell, and the nickel 10 content in the compartments (2) is maintained at the desired value for optimum deposition conditions. Such control is readily achieved on the basis of the known difference between the cathode and anode current efficiencies of the nickel bath. If that difference is, for example, 5%, the device (34) controls the current value of the electrolytic cell (26) so that it reaches 5% of the amount of the current consumed 15 in the treating stations of the nickel bath (1).

20 CLAIMS

1. A process for the electrodeposition of nickel onto articles which are subsequently rinsed, in which a proportion of the nickel electrolyte is continuously removed from the electrodeposition bath, a part of the removed electrolyte is combined with used liquid from the rinsing apparatus and passed through filtration means for reducing the concentration of organic decomposition products; the filtrate is combined 25 with the remainder of the removed nickel electrolyte, a major proportion of the resulting mixture is recirculated directly to the electrodeposition bath, a minor proportion of the said resulting mixture is passed through purification means comprising, in sequence, 30 means for removing impurity metals from solution, and thereafter electrolytic means for recovering nickel, the purified solution so obtained is recirculated to the electrodeposition bath, and the introduction of fresh rinsing liquid into the rinsing station is controlled so as to counterbalance evaporation losses in the electrodeposition bath and in the filtration and purification means.
2. A process as claimed in claim 1, wherein the filtration means for organic decomposition products 40 comprises an activated carbon filter.
3. A process as claimed in claim 2, wherein the activated carbon filter is so constructed that the solution to be filtered flows therethrough as a result of a geodesic difference in levels.
4. A process as claimed in any one of claims 1 to 50 3, wherein the impurity metals are removed by preferential electrodeposition.
5. A process as claimed in any one of claims 1 to 4, wherein the rinsing is effected in a multiple cascade rinsing apparatus.
6. A process as claimed in any one of claims 1 to 55 5, wherein the current to the electrolytic nickel-recovery means is so controlled in accordance with the current consumption in the electrodeposition bath that only the excess nickel dissolved in the bath is removed in the nickel-recovery means.
7. A process as claimed in any one of claims 1 to 60 6, wherein the cathode elements in the nickel-recovery means are so designed that the deposited nickel accumulates in the form of discrete pieces.

8. A process as claimed in any one of claims 1 to 7, wherein the solutions that are recirculated to the electrodeposition bath are filtered to remove solid contaminants.

9. A process for the electrodeposition of nickel, conducted substantially as described herein with reference to the accompanying drawings.
10. Apparatus for the electrodeposition of nickel, which comprises an electrodeposition bath, means 75 for rinsing articles after electrodeposition, means for continuously removing a proportion of the electrolyte in the electrodeposition bath, means for combining a part of the removed electrolyte with used liquid from the rinsing means, filtration means for reducing the concentration of organic decomposition products in the resulting mixture, means for combining the filtrate with the remainder of the removed electrolyte, means for recirculating a major proportion of the resulting mixture directly to the electrodeposition bath, purification means for treating a minor proportion of the said resulting mixture firstly to remove impurity metals from the solution and thereafter to recover a proportion of nickel electrolytically, means for recirculating the resulting purified solution to the electrodeposition bath, and means for introducing fresh rinsing liquid into the rinsing apparatus so as to counterbalance evaporation losses in the electrodeposition bath and in the filtration and purification means.
11. Apparatus as claimed in claim 10, which includes means for controlling the introduction of rinsing liquid in accordance with the liquid level in the electrolytic nickel-recovery means.

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